

FORM PTO-1390
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

1576.98

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/070321

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/JP00/05958

01 September 2000 (1.09.00)

03 September 1999 (3.09.99)

TITLE OF INVENTION ALKENYLPHENOL COPOLYMER AND PROCESS FOR PRODUCING THE SAME

APPLICANT(S) FOR DO/EO/US

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
- a. ☐ is attached hereto (required only if not communicated by the International Bureau).
- b. ☒ has been communicated by the International Bureau.
- c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
- a. ☒ is attached hereto.
- b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
- a. ☐ are attached hereto (required only if not communicated by the International Bureau).
- b. ☐ have been communicated by the International Bureau.
- c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
- d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Copy of Form PCT/1B/304; Copy of Form PCT/ISA/210 (International Search Report); Copy of PCT Application (Japanese); Copy of Preliminary Examination (Japanese); Copy of WO 01/18083 A1 (Japanese)

U.S. APPLICATION NO. (if known, see 37 CFR 1.57)

10/070321

INTERNATIONAL APPLICATION NO.

PCT/JP00/05958

ATTORNEY'S DOCKET NUMBER

1576.98

21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)
 nor international search fee (37 CFR 1.445(a) (2)) paid to USPTO
 and International Search Report not prepared by the EPO or JPO \$1000.00

International preliminary examination fee (37 CFR 1.482) not paid to
 USPTO but International Search Report prepared by the EPO or JPO \$860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
 but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
 but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
 and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ 890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	6 -20 =	0	x \$18.00	\$ 0.00
Independent claims	1 -3 =	0	x \$80.00	\$ 0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$ 0.00

TOTAL OF ABOVE CALCULATIONS =

\$ 890.00

☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
 are reduced by 1/2.

+ \$ 0.00

SUBTOTAL =

\$ 890.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
 months from the earliest claimed priority date (37 CFR 1.492(f)).

\$ 0.00

TOTAL NATIONAL FEE =

\$ 890.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
 accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$ 0.00

TOTAL FEES ENCLOSED =

\$ 890.00

Amount to be
refunded:

\$

charged:

\$

- a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-1992 in the amount of \$ 890.00 to cover the above fees.
 A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. 13-1992. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card
 information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Dennis G. LaPointe
 Mason & Associates, P.A.
 17757 US Hwy 19 N., Suite 500
 Clearwater, FL 33764


 SIGNATURE

Dennis G. LaPointe
 NAME

40,693
 REGISTRATION NUMBER

Practitioner's Docket No. 1576.98

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: MATSUMOTO et al, Hitoshi

Application No.: Unknown

Group No.: n/a

Filed: 03/01/2002

Examiner: n/a

For: ALKENYLPHENOL COPOLYMER AND PROCESS FOR PRODUCING THE SAME

DO/EO/US

Assistant Commissioner for Patents

Washington, D.C. 20231

EXPRESS MAIL CERTIFICATE

"Express Mail" label number EV 032346025 US

Date of Deposit 03/01/2002

I hereby state that the following *attached* paper or fee

- Transmittal Letter To The DO/EO/US
- Combined Declaration and Power Of Attorney
- Specifications, Claims, Abstract
- Copy of Form PCT/IB/304; Copy of International Search Report; Copy of PCT Application (Japanese); Copy of Preliminary Examination (Japanese); Copy of WO 01/18083 AI (Japanese)
- Express Mail Certificate and Post card

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. section 1.10, on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Lia H. Costello, Legal Asst.



Signature of person mailing paper or fee

10/070321

JC19 Rec'd PGT/PTO 01 MAR 2002

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Hitoshi MATSUMOTO et al.)
S.N.:) Examiner: UNKNOWN
Filed:) Art Unit: UNKNOWN
For: ALKENYLPHENOL COPOLYMER AND)
PROCESS FOR PRODUCING THE SAME)

Box Patent Application
Hon. Commissioner of Patents
Washington, D.C. 20231

Dear Sir:

Please amend the above-identified patent application prior to examination thereof in the manner indicated below.

PRELIMINARY AMENDMENT
(37 C.F.R. §1.111)

IN THE CLAIM:


Please amend claim 3. A marked-up version of the amended claim is attached herein on a separate sheet and clean version of the amended claim is also attached herein on a separate sheet.

Please add new claims 5-6. The new claims also are attached herein on a separate sheet.

The amended claim 3 and new claims 5-6 are intended to eliminate the multi-dependent claims.

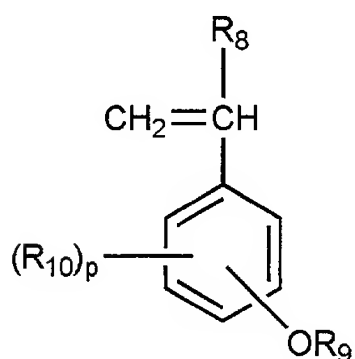
Very respectfully,

Dated: 2/25/02


Dennis G. LaPointe
MASON & ASSOCIATES, P.A.
17757 U.S. Hwy. 19 North
Mangrove Bay, Suite 500
Clearwater, FL 33764
(727) 538-3800
Reg. #40,693

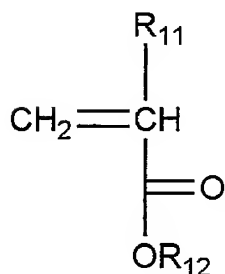
MARKED-UP VERSION OF AMENDED CLAIM 3

3. (Amended) A process for the preparation of the alkenylphenol copolymer according to Claim 1 [or 2] in which a compound represented by Formula (IV) whose hydroxyl group of the phenol residue is protected



Formula (IV)

(wherein, R_8 is hydrogen or methyl, R_9 is a group to be eliminated and/or decomposed with an acid, R_{10} is alkyl having 1 to 5 carbons, p is 0, 1 or 2 and R_{10} is the same or different when p is 2) is polymerized, or a compound of Formula (IV) and a vinylaromatic compound are copolymerized, by anionic polymerization using an anionic polymerization initiator as a polymerization initiator, followed by copolymerization with a (meth)acrylic ester represented by Formula (V)

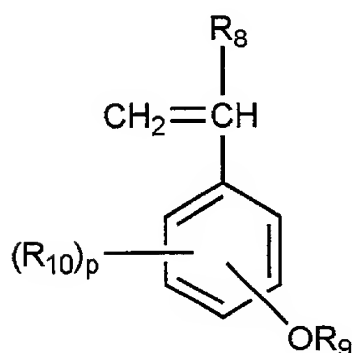


Formula (V)

(wherein, R_{11} is hydrogen or methyl, and R_{12} is a group having a t-butyl group and to be eliminated and/or decomposed with an acid); and the obtained block copolymer is treated with an acid reagent to eliminate and/or decompose only a specified amount of the group protecting the phenolic hydroxyl group.

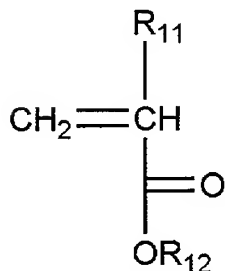
CLEAN VERSION OF AMENDED CLAIM 3

3. (Amended) A process for the preparation of the alkenylphenol copolymer according to Claim 1 in which a compound represented by Formula (IV) whose hydroxyl group of the phenol residue is protected



Formula (IV)

(wherein, R₈ is hydrogen or methyl, R₉ is a group to be eliminated and/or decomposed with an acid, R₁₀ is alkyl having 1 to 5 carbons, p is 0, 1 or 2 and R₁₀ is the same or different when p is 2) is polymerized, or a compound of Formula (IV) and a vinylaromatic compound are copolymerized, by anionic polymerization using an anionic polymerization initiator as a polymerization initiator, followed by copolymerization with a (meth)acrylic ester represented by Formula (V)

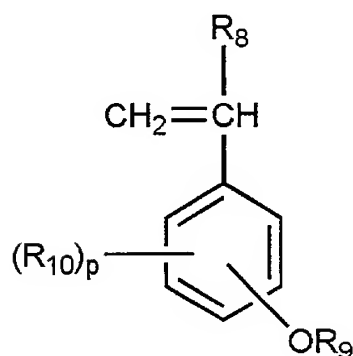


Formula (V)

(wherein, R_{11} is hydrogen or methyl, and R_{12} is a group having a t-butyl group and to be eliminated and/or decomposed with an acid); and the obtained block copolymer is treated with an acid reagent to eliminate and/or decompose only a specified amount of the group protecting the phenolic hydroxyl group.

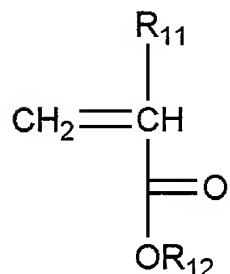
NEW CLAIMS

5. A process for the preparation of the alkenylphenol copolymer according to Claim 2 in which a compound represented by Formula (IV) whose hydroxyl group of the phenol residue is protected



Formula (IV)

(wherein, R_8 is hydrogen or methyl, R_9 is a group to be eliminated and/or decomposed with an acid, R_{10} is alkyl having 1 to 5 carbons, p is 0, 1 or 2 and R_{10} is the same or different when p is 2) is polymerized, or a compound of Formula (IV) and a vinylaromatic compound are copolymerized, by anionic polymerization using an anionic polymerization initiator as a polymerization initiator, followed by copolymerization with a (meth)acrylic ester represented by Formula (V)



Formula (V)

(wherein, R_{11} is hydrogen or methyl, and R_{12} is a group having a t-butyl group and to be eliminated and/or decomposed with an acid); and the obtained block copolymer is treated with an acid reagent to eliminate and/or decompose only a specified amount of the group protecting the phenolic hydroxyl group.

6. A process for the preparation of the alkenylphenol copolymer according to Claim 5 in which the step of eliminating and/or decomposing only a specified amount of the group protecting the phenolic hydroxyl group with an acid reagent is carried out at below 60°C.

Specification

ALKENYLPHENOL COPOLYMER AND PROCESS FOR PRODUCING THE SAME

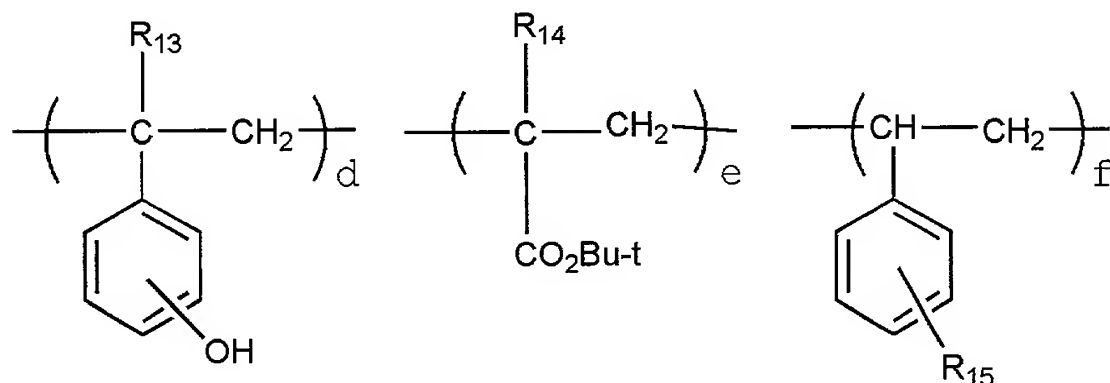
Technical Fields:

The present invention relates to narrow-disperse alkenylphenol copolymers that have not known yet and to processes for the preparation of the same. In more detail, it relates to narrow-disperse alkenylphenol copolymers that have controlled structures and with alkenylphenol units, alkenylphenyl ether units and (meth)acrylic ester units as essential constituent units, and to processes for the preparation of the same. The alkenylphenol copolymers of the present invention have expectations to be used as resist materials for excimer lasers.

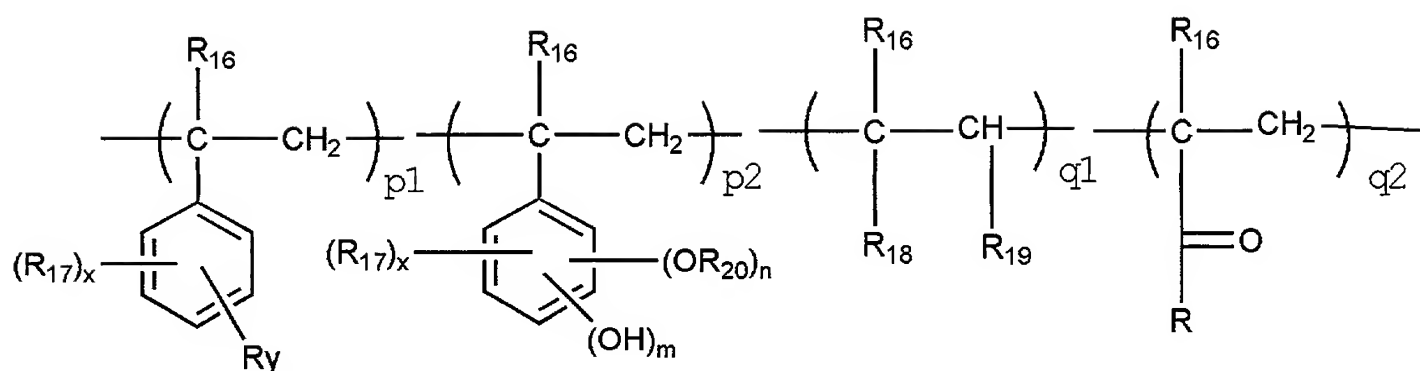
Background Art:

Alkenylphenol copolymers useful as resist materials have been well known so far. For example, Japanese Patents Laid-open Nos. Hei 4-211258, 7-209868, 7-49569, 9-160244 and 11-125907 describe random copolymers containing repeating units represented by Formulae (I), (II) and (III). Japanese Patent Laid-open No. Hei 11-125907 describes positive-type radiation-sensitive resin compositions that have, as constituents, resins insoluble or hardly soluble in alkali and protected with groups to be dissociated with acids. The resins become soluble in alkali when the said acid dissociating groups are dissociated. It

describes, as constituent units of the said resins, random copolymers or block copolymers each having constituent units represented by Formula (IV) (wherein, R_{13} and R_{14} are each independently hydrogen or methyl, and R_{15} is hydrogen, t-butoxy or another group).

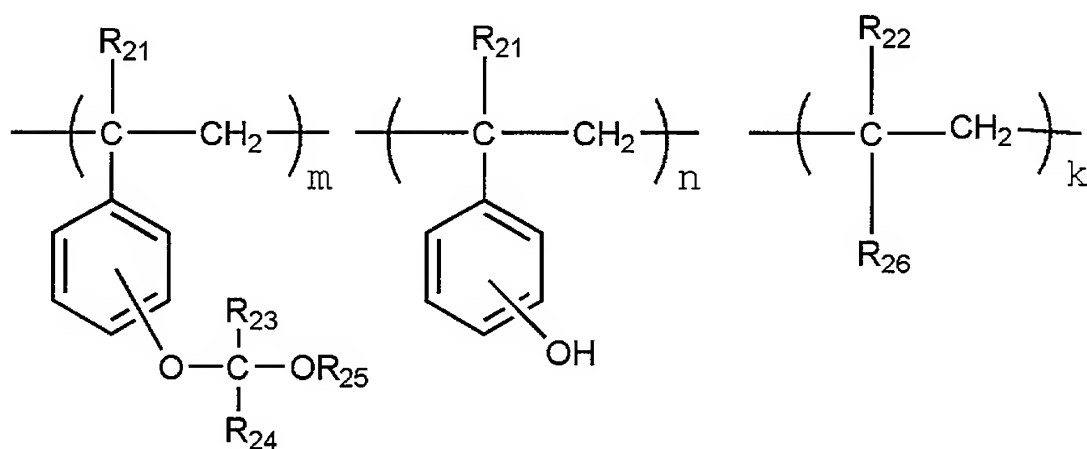


Japanese Patent Laid-open No. Hei 10-265524 describes a polymer compound having a repeating unit represented by Formula (VII) shown below (wherein, R is hydroxyl or OR_{20} , and R_{20} is a group unstable to acids). The polymer is cross-linked by a cross-linking group with an intramolecular and/or intermolecular C-O-C groups that are obtained by a reaction of part of the phenolic hydroxyl group and/or carboxyl group, which are represented by R of Formula (VII), with an alkenyl ether compound or halogenated alkyl ether. The polymer has the weight-average molecular weight of 1,000 to 500,000, with the total amount of the said acid-unstable groups and cross-linking groups at a ratio exceeding 0 mole% and less than 80 mole% of the average of the whole phenolic hydroxyl and carboxyl groups.



Formula (VII)

Japanese Patent Laid-open No. Hei 10-53621 describes polymers having a structure represented by Formula (VIII) (wherein, R_{21} is hydrogen or lower alkyl, R_{23} and R_{24} are hydrogen, alkyl optionally substituted with halogen or another, R_{25} is alkyl optionally substituted with halogen or another, and R_{26} is carboxyl optionally substituted with alkyl or another), with dispersibility of more than 1 and less than 1.5.



Formula (VIII)

Disclosure of the Invention:

Homopolymers and copolymers of alkenylphenols, represented by poly-p-hydroxystyrene and the like, are useful as materials for chemical amplification type resists for excimer lasers. Among them, particularly resists

produced using copolymers consisting of hydroxystyrenes and acrylic esters are known as so-called ESCAP type resists able to give higher resolution.

In this field, technology to make resolution higher has been advanced remarkably, and higher resolution is always looked for. A desirable structure for the ESCAP type polymers to realize higher resolution is a structure with groups that protect part of the alkenylphenol portions and are eliminated and/or decomposed with acids produced when the groups are exposed to light. Besides, a desirable polymer has a narrow molecular distribution and a controlled structure. This kind of structure controls unnecessary, excessive diffusion of acids generated from photoacid generators of a resist composition, and the solubility of the phenolic hydroxyl or carboxyl groups is controlled so as not to dissolve excessively in alkali developers. Thanks to these effects, the obtained polymer is expected to be a resist material to contribute to make resolution higher.

Many of ESCAP type polymers with such structures and which have been reported so far are synthesized by radical polymerization, and are not satisfactory because of the dispersibility (M_w/M_n) of more than 1.50. The said Japanese Patent Laid-open No. Hei 10-265524 has disclosed an ESCAP type polymer having a narrow molecular distribution and a controlled structure. The polymer is unsatisfactory, however, because the ester portion as a protecting group is a group that is not eliminated with an acid, such as

20250401 10:00:00
methyl, or that has a carboxylic acid residue. With such an ester structure, it is difficult to make solubility in an alkali developer different between an area exposed to light and that not exposed. Besides, a method is applied of introducing the said group protecting the hydroxyl or carboxylic acid group partially at a later stage. Because of it, there is a problem of difficulty to completely protect particularly the carboxylic acid portions in the polymer.

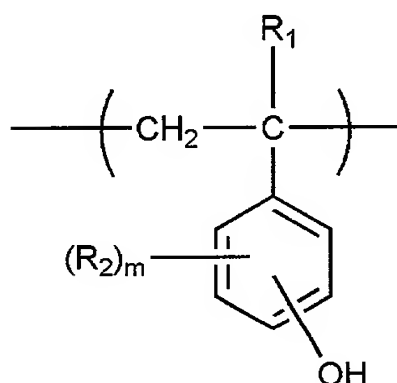
The said Japanese Patent Laid-open No. Hei 11-125907 describes random copolymers or block copolymers, but has no description of synthetic methods and molecular distributions of these polymers. The said Japanese Patent Laid-open No. Hei 10-53621 has disclosed ESCAP type polymers with narrow dispersibility, but actually described only random copolymers, which were not satisfactory as materials for high resolution resists.

It is an object of the present invention to provide narrow-disperse, ESCAP type polymers that do not contain carboxylic acid residues, have controlled structures, and have groups protecting phenolic hydroxyl groups and being eliminated and/or decomposed with acids selectively and partially.

The inventors of the present invention have studied in earnest to accomplish the above object and found that block copolymerization consisting of alkenylphenols with protected phenolic hydroxyl groups or the said alkenylphenols and vinylaromatic compounds, with

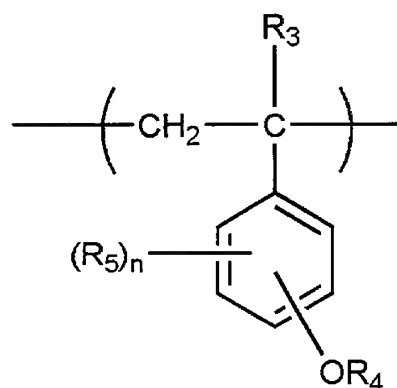
(meth)acrylic esters results in eliminating and/or decomposing the groups protecting the phenolic hydroxyl groups with acids selectively and partially. It was confirmed that alkenylphenol copolymers with narrow molecular distributions and controlled structures could be synthesized from the said block copolymers. Thus the present invention has been completed.

The present invention relates to alkenylphenol copolymers that Component (A) containing a repeating unit represented by Formula (I)



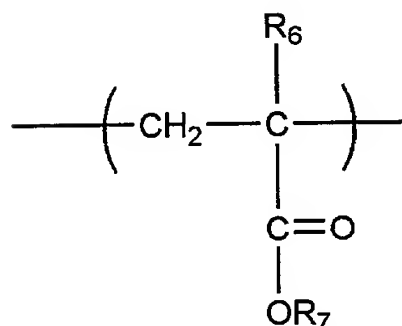
Formula (I)

(wherein, R_1 is hydrogen or methyl, R_2 is alkyl having 1 to 5 carbons, m is 0, 1 or 2 and R_2 is the same or different when m is 2) and a repeating unit represented by Formula (II)



Formula (II)

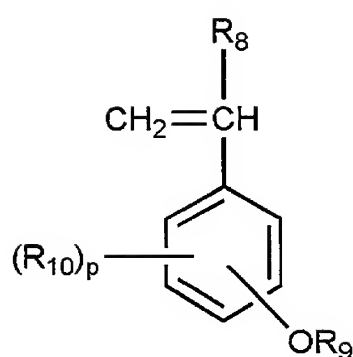
(wherein, R₃ is hydrogen or methyl, R₄ is a group to be eliminated and/or decomposed with an acid, R₅ is alkyl having 1 to 5 carbons, n is 0, 1 or 2 and R₅ is the same or different when n is 2), and Component (B) containing a repeating unit represented by Formula (III)



Formula (III)

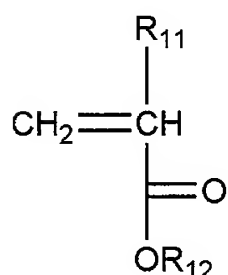
(wherein, R₆ is hydrogen or methyl, and R₇ is a group having a t-butyl group and to be eliminated and/or decomposed with an acid) are bound in block in the (A)-(B) form, and that have a ratio (Mw/Mn) of the weight-average molecular weight (Mw) to the number-average molecular weight (Mn) in a range of 1.00 and 1.50 and without carboxylic acid residues. It also relates to the said alkenylphenol copolymers with weight-average molecular weight of 1,000 to 100,000.

The present invention relates to a process for the preparation of the said alkenylphenol copolymer, characterized by that a compound represented by Formula (IV) with the protected hydroxyl group of the phenol residue



Formula (IV)

(wherein, R_8 is hydrogen or methyl, R_9 is a group to be eliminated and/or decomposed with an acid, R_{10} is alkyl having 1 to 5 carbons, p is 0, 1 or 2 and R_{10} may be the same or different when p is 2) is polymerized, or a compound of Formula (IV) and a vinylaromatic compound are copolymerized, by anionic polymerization using an anionic polymerization initiator as a polymerization initiator, followed by copolymerization with a (meth)acrylic ester represented by Formula (V)



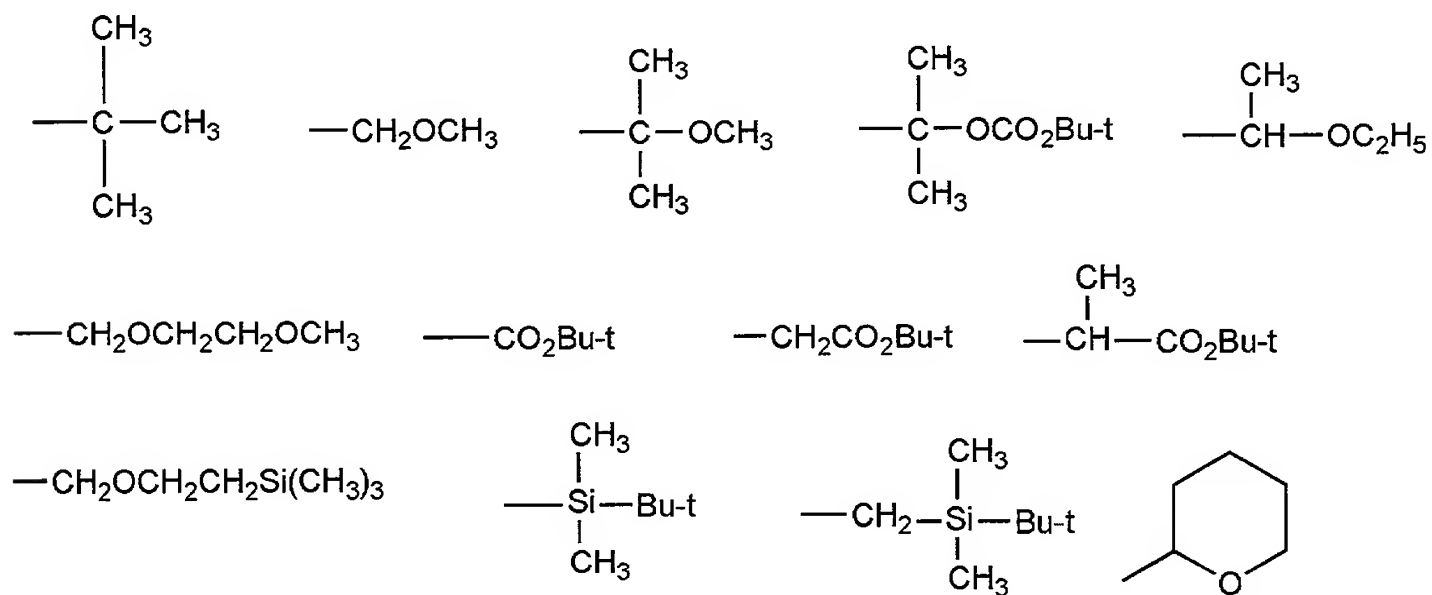
Formula (V)

(wherein, R_{11} is hydrogen or methyl, and R_{12} is a group having a t-butyl group and to be eliminated and/or decomposed with an acid); and the obtained block copolymer is treated with an acid reagent to eliminate and/or decompose only a specified amount of the group protecting the phenolic hydroxyl group. The present invention also

relates to a process for the preparation of the said alkenylphenol copolymer, characterized by that only a specified amount of the group protecting the phenolic hydroxyl group is eliminated and/or decomposed with an acid reagent at a temperature below 60°C.

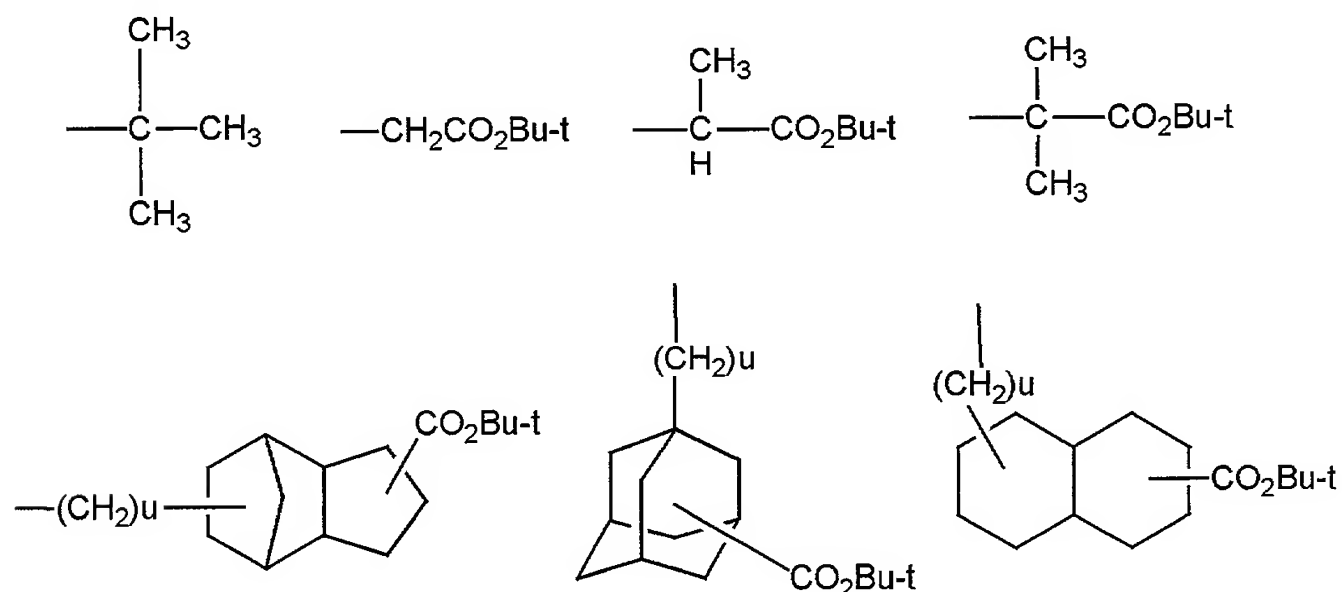
In the "repeating unit of Formula (I)" of the present invention, R₁ is hydrogen or methyl. R₂ is alkyl having 1 to 5 carbons. Examples of the alkyl group having 1 to 5 carbons include methyl, ethyl, n-propyl, isopropyl, n-butyl and t-butyl. m is 0, 1 or 2. When m is 2, R₅ is the same or different. Positions of hydroxyl (OH) group and R₂ are not specifically restricted. The hydroxyl group is preferably at the para or meta position of the alkenyl group.

In the "repeating unit of Formula (II)" of the present invention, R₃ is hydrogen or methyl. R₄ is a group to be eliminated and/or decomposed with an acid. Examples of the group to be eliminated and/or decomposed with an acid include functional groups such as those represented by the following formulae.



R₅ is alkyl having 1 to 5 carbons. Examples of the alkyl group having 1 to 5 carbons include methyl, ethyl, n-propyl, isopropyl, n-butyl and t-butyl. n is 0, 1 or 2. When n is 2, R₅ is the same or different. Substitution positions of the alkoxy (OR₄) group and R₅ are not specifically restricted. The alkoxy (OR₄) group is preferably at the para or meta position of the alkenyl group.

In the "repeating unit of Formula (III)" of the present invention, R₆ is hydrogen or methyl. R₇ is a group having a t-butyl group and to be eliminated and/or decomposed with an acid. Examples of the groups having a t-butyl group and to be eliminated and/or decomposed with an acid include functional groups such as those represented by the following formulae (wherein, u is 0 or 1).

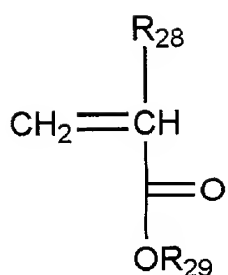


The polymers of the present invention may contain repeating units other than those represented by Formulae

(I) to (III), if required. There are no particular restrictions on the repeating units if the units are produced from compounds having double bonds copolymerable with monomers corresponding to Formulae (I) to (III). Preferred are repeating units with no acidic substituents such as sulfonic acid group, carboxyl group and phenolic hydroxyl group. Examples of monomers corresponding to the said repeating units include compounds containing vinyl groups and compounds containing (meth)acryloyl groups.

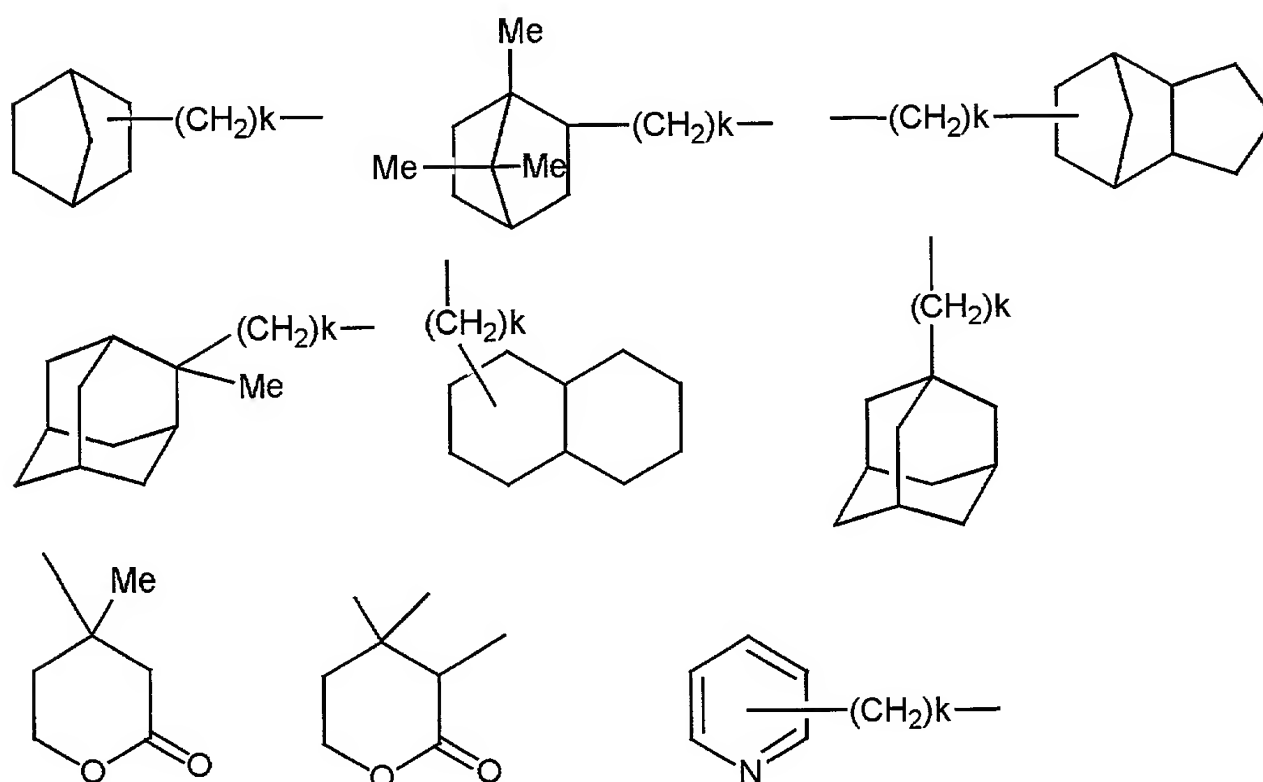
Examples of the said compounds containing vinyl groups include aromatic vinyl compounds such as styrene, α -methylstyrene, chlorostyrene, 1,1-diphenylethylene and stilbene; aromatic vinyl compounds containing hetero atoms such as vinylpyridine; vinyl ketone compounds such as methyl vinyl ketone and ethyl vinyl ketone; vinyl ether compounds such as methyl vinyl ether and ethyl vinyl ether; and alicyclic vinyl compounds containing hetero atoms such as vinyl pyrrolidone and vinyl lactam.

Examples of the said compounds containing (meth)acryloyl groups include (meth)acrylic esters represented by Formula (IX) (wherein, R_{28} is hydrogen or methyl, R_{29} is alkyl having 1 to 12 carbons, hydrocarbon group having an alicyclic structure of 3 or more carbons, hydrocarbon group that has an alicyclic structure containing hetero atoms and having 2 or more carbons, or heteroaryl), or (meth)acrylonitrile.



Formula (IX)

Examples of R_{29} of Formula (IX) include methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-octyl, n-decyl or functional groups represented by the following formulae (wherein, k is 0 or 1).



These compounds containing vinyl groups or containing (meth)acryloyl groups can be used alone or as a mixture of two or more. Repeating units obtained from these compounds containing vinyl groups or containing (meth)acryloyl groups can be contained in the alkenylphenol copolymers of the present invention by random or block copolymerization with

repeating units of Formulae (I) to (III). An example of Component (A) containing a repeating unit represented by Formula (I) and that of Formula (II) includes Component (A) containing additional repeating units corresponding to styrene, α -methylstyrene and the like as monomers. In this case, in Component A, a mole ratio of the repeating unit of Formula (I) to the total of the repeating unit of Formula (II) and the repeating unit corresponding to styrene or the like as a monomer is preferably in the range of 99/1 to 50/50.

The alkenylphenol copolymers of the present invention are characterized by block copolymerization of Component (A) containing the repeating units of alkenylphenol represented by Formulae (I) and (II) with Component (B) containing the repeating unit of (meth)acrylic ester represented by Formula (III), in the form of (A) \square (B). Actual examples of the alkenylphenol copolymers of the present invention follow:

- Poly[p-t-butoxystyrene/p-hydroxystyrene/t-butyl (meth)acrylate],
- Poly[p-t-butoxy- α -methylstyrene/p-hydroxystyrene/t-butyl (meth)acrylate],
- Poly[p-t-butoxystyrene/p-hydroxy- α -methylstyrene/t-butyl (meth)acrylate],
- Poly[m-t-butoxystyrene/m-hydroxystyrene/t-butyl (meth)acrylate],
- Poly[p-t-butoxystyrene/p-hydroxystyrene/t-butyl

methacrylate/t-butyl acrylate],

- Poly[p-t-butoxystyrene/p-hydroxystyrene/t-butyl (meth)acrylate/isobonyl (meth)acrylate],
- Poly[p-t-butoxystyrene/p-hydroxystyrene/dicyclopentenyl (meth)acrylate/t-butyl (meth)acrylate],
- Poly[p-(1-ethoxyethoxy)styrene/p-hydroxystyrene/t-butyl (meth)acrylate],
- Poly[p-t-butoxystyrene/p-hydroxystyrene/t-butoxycarbonylmethyl (meth)acrylate].
- Poly[p-(tetrahydropyranyloxy)styrene/p-hydroxystyrene/t-butyl (meth)acrylate],
- Poly[p-t-butoxystyrene/p-(tetrahydropyranyloxy)styrene/p-hydroxystyrene/t-butyl (meth)acrylate], and
- Poly[p-t-butoxystyrene/styrene/p-hydroxystyrene/t-butyl (meth)acrylate]

A ratio (M_w/M_n) of weight-average molecular weight (M_w) to number-average molecular weight (M_n), which represents the dispersibility of the alkenylphenol copolymers of the present invention, is in the range of 1.00 to 1.50, preferably 1.00 to 1.20. The weight-average molecular weight (M_w) is preferably in the range of 1,000 to 100,000, and more preferably 1,000 to 30,000. A mole ratio [(A)/(B)] of Component (A) to Component (B) is preferably in the range of 95/5 to 5/95, more preferably 95/5 to 70/30. There are no particular restrictions on mole ratios of the repeating unit of Formula (I) to that of Formula (II), which compose Component (A). It is preferable in the range

of 99.5/0.5 to 50/50, and more preferably 95/5 to 60/40.

Of the compound of Formula (IV) used for the preparation of the alkenylphenol copolymers of the present invention, R_8 is hydrogen or methyl, R_9 is a group to be eliminated and/or decomposed with an acid, R_{10} is alkyl having 1 to 5 carbons, and p is 0, 1 or 2. R_{10} is the same or different when p is 2. R_9 corresponds to R_4 in Formula (II), and R_{10} to R_5 in Formula (II). Their actual examples are aforementioned.

Examples of the compounds of Formula (IV) include p-t-butoxystyrene, p-t-butoxy- α -methylstyrene, m-t-butoxystyrene, m-t-butoxy- α -methylstyrene, p-(tetrahydropyranyloxy)styrene, p-(tetrahydropyranyloxy)- α -methylstyrene, p-(1-ethoxyethoxy)styrene and p-(1-ethoxyethoxy)- α -methylstyrene. These can be used alone or as a mixture of two or more.

Examples of vinylaromatic compounds used for the preparation of the alkenylphenol copolymers of the present invention include styrene, o-methylstyrene, p-methylstyrene, p-t-butylstyrene, α -methylstyrene, 1,3-butylstyrene, 1,1-diphenylethylene and stilbene. These can be used alone or as a mixture of two or more.

Of the (meth)acrylic esters of Formula (V) used for the preparation of the alkenylphenol copolymers of the present invention, R_{11} is hydrogen or methyl, R_{12} is a group having a t-butyl group and to be eliminated and/or decomposed with an acid. R_{12} corresponds to R_7 in

Formula (III). Its actual examples are aforementioned.

Examples of the compounds of Formula (V) include t-butyl (meth)acrylate, t-butoxycarbonylmethyl (meth)acrylate and 1-methyl-t-butoxycarbonylmethyl (meth)acrylate. These can be used alone or as a mixture of two or more.

To produce an alkenylphenol copolymer of the present invention, first anionic polymerization of a compound of Formula (IV) alone, or a compound of Formula (IV) and a vinylaromatic compound, is carried out with an anionic polymerization initiator used as a polymerization initiator, followed by a block copolymerization reaction by adding a (meth)acrylic ester of Formula (V) to the reaction system. The reaction is usually carried out under the atmosphere of inert gas, such as nitrogen or argon, in an organic solvent at -100 to 50°C, preferably -100 to 0°C, more preferably -100 to -20°C.

Examples of anionic polymerization initiators used for the said anionic polymerization include alkali metals and organic alkali metals. Examples of the alkali metals include lithium, sodium, potassium and cesium. Examples of the organic alkali metals include alkyl, allyl and aryl compounds of the above alkali metals. These anionic polymerization initiators can be used alone or as a mixture of two or more. Examples of the organic alkali metals include ethyl lithium, n-butyl lithium, sec-butyl lithium, t-butyl lithium, ethyl sodium, lithium biphenyl, lithium naphthalene, lithium triphenyl, sodium naphthalene, α -methylstyrene sodium dianion, 1,1-diphenylhexyl lithium and

1,1-diphenyl-3-methylpentyl lithium.

Examples of organic solvents used for the said polymerization reactions include aliphatic hydrocarbons such as n-hexane and n-heptane; alicyclic hydrocarbons such as cyclohexane and cyclopentane; aromatic hydrocarbons such as benzene and toluene; and ethers such as diethyl ether, tetrahydrofuran and dioxane, as well as those usually used for anionic polymerization such as anisole and hexamethylphosphoramide. These are used alone or as a mixed solvent of two or more. A combination of polar solvents and non-polar solvents is particularly preferred. It is more favorable to combine ethers with aromatic or aliphatic hydrocarbons.

When copolymerization is carried out with a (meth)acrylic ester added, an addition of an alkali metal salt and/or alkaline earth metal salt of a mineral acid can control the polymerization reaction. Lithium chloride is particularly preferred to use as the alkali metal salt and/or alkaline earth metal salt of a mineral acid.

From a copolymer thus obtained, a certain amount of the group protecting the phenolic hydroxyl group is eliminated and/or decomposed with an acid reagent, to form the alkenylphenol structure. Examples of solvents used for the elimination/decomposition reaction include alcohols such as methanol and ethanol; ketones such as acetone and methyl ethyl ketone; polyhydric alcohol derivatives such as methyl cellosolve and ethyl cellosolve; and water, in addition to those exemplified for the above polymerization reactions.

These may be used alone or as a mixture of two or more.

There are no particular restrictions on acid reagents used. Actual examples of the acid reagents include hydrochloric acid, sulfuric acid, hydrogen chloride gas, phosphoric acid, hydrobromic acid, p-toluenesulfonic acid, 1,1,1-trifluoroacetic acid, methanesulfonic acid, trifluoromethanesulfonic acid and hydrogen sulfates represented by Formula $XHSO_4$ (wherein, X is an alkali metal such as Li, Na or K). A catalytic amount is sufficient to use. Usually, the mole fraction of each unit and the average molecular weight of the whole polymer from the molecular weight of each unit are calculated. The mole number of each unit is calculated from the total weight, average molecular weight and mole fraction of the polymer. An amount of acid reagent used is in the range of 0.1 to 3 equivalents, preferably 0.1 to 1 equivalent, to the mole number of the alkenylphenol unit.

The elimination reaction of the protecting group is usually carried out at room temperature to 150°C. It is however carried out in the range of room temperature and below 70°C, preferably room temperature and below 60°C, and more preferably 30°C and 50°C, in order to control the hydrolysis of the (meth)acrylic ester portion when the phenolic hydroxyl group is deprotected. The hydrolysis of the ester portion can be controlled even if the reaction is carried out at above 60°C, if the (meth)acrylic ester has a bulky substituent such as alicyclic group having 7 or more carbons or alkyl having an alicyclic group.

In the deprotection reaction, appropriate combinations between a type and concentration of a solvent, type and addition amount of a catalyst, and a reaction temperature and reaction time can control the hydrolysis of the (meth)acrylic ester and deprotection of the phenolic hydroxyl group. For example, the elimination reaction rate can be controlled in a way that a reaction is carried out keeping a temperature at 60°C at the initial stage of the reaction to remove 80 to 90% of the specified amount, and the reaction temperature is then lowered and, if necessary, water is added to adjust the acid concentration. As a result, a target product can be obtained at the accuracy of about $\pm 1\%$ to the specified amount.

To eliminate only a desired, specified amount of the protecting group, the reaction is tracked as required, and the reaction is stopped when the specified amount is eliminated. Examples of means to track the reaction include IR spectra or methods of measuring changes in polymer solubility.

Best Form to Implement the Invention:

The present invention is described in more detail in reference to Examples. The scope of the present invention, however, is not restricted at all by the following examples.

Example 1

Under a nitrogen atmosphere, 1500g of tetrahydrofuran

(THF) was kept at -60°C , and 30 mmol of n-butyl lithium (NBL) was added. A mixture of 0.8 mol of p-t-butoxystyrene (PTBST) and 0.2 mol of styrene (St) was added dropwise with stirring over an hour. The reaction was continuously carried out further for an hour. The completion of the reaction was confirmed by gas chromatography (GC). Then, 0.5 mol of t-butyl methacrylate (t-BMA) was added dropwise over 30 minutes. The reaction was continuously carried out further for an hour. GC confirmed the completion of the reaction. Methanol was added to the reaction system to stop the reaction. The reaction solution was poured into a large amount of methanol. The deposited polymer was filtrated, washed and dried at 60°C under reduced pressure for 5 hours to give white powder polymer. The polymerization yield to the total amount of the monomers used was 99.5%.

An analysis by gel permeation chromatography (GPC) showed that the polymer was a narrow-disperse polymer with $M_n = 8,600$ and $M_w/M_n = 1.17$. The copolymerization ratio calculated from ^{13}C -NMR spectra was PTBST unit/St unit/t-BMA unit = $0.8/0.2/0.5$ (mole ratio). Based on these facts, it was confirmed that the copolymerization reactions proceeded with no side reactions and the designed copolymer was produced.

10g of the obtained polymer was dissolved in a mixed solvent of THF/ethanol = 4/1 (ratio by weight) to make a 25% solution. After the solution was heated to 40°C , 3g of concentrated hydrochloric acid was added to the reaction system to initiate the debutylation reaction. A small

volume of the solution was collected from the reaction system and analyzed by IR spectra, as required, in order to track the reaction. When it was confirmed that the specified amount was eliminated, the reaction system was promptly cooled in an ice-water bath. The reaction solution was poured into a large amount of water. The deposited polymer was filtrated, washed and dried at 60°C under reduced pressure for 5 hours to give 7.7g of white powder polymer.

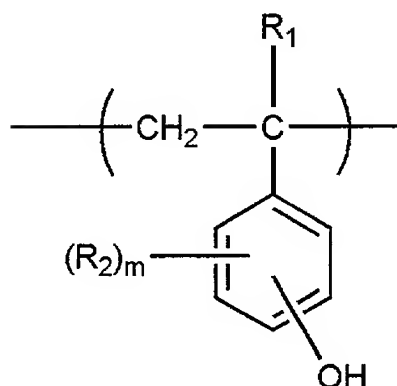
An analysis by GPC showed that the polymer was a narrow-disperse polymer with $M_n = 7900$ and $M_w/M_n = 1.16$. The copolymerization ratio calculated from ^{13}C -NMR spectra was PTBST unit/vinyl phenol (PHS) unit/St unit/t-BMA unit = 0.4/0.4/0.2/0.5 (mole ratio).

Industrial Applicability:

According to the present invention, a copolymer of an alkenylphenol having the hydroxyl group protected, with a (meth)acrylic ester is synthesized using anionic polymerization and the phenolic hydroxyl group is then selectively eliminated. As a result, an ESCAP type alkenylphenol copolymer can be synthesized that has a controlled structure, is a narrow-disperse polymer with the phenolic hydroxyl group protected partially, and has better resolution than that of known polymers in terms of a resist material for KrF excimer lasers.

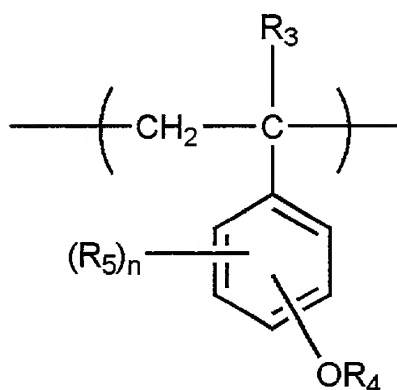
What Is Claimed:

1. An alkenylphenol copolymer characterized by that a copolymer consists of Component (A) containing a repeating unit represented by Formula (I)



Formula (I)

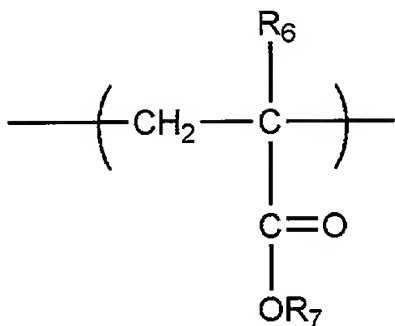
(wherein, R₁ is hydrogen or methyl, R₂ is alkyl having 1 to 5 carbons, m is 0, 1 or 2 and R₂ is the same or different when m is 2) and a repeating unit represented by Formula (II)



Formula (II)

(wherein, R₃ is hydrogen or methyl, R₄ is a group to be eliminated and/or decomposed with an acid, R₅ is alkyl having 1 to 5 carbons, n is 0, 1 or 2 and R₅ is the same or different when n is 2) and Component (B) containing a

repeating unit represented by Formula (III)

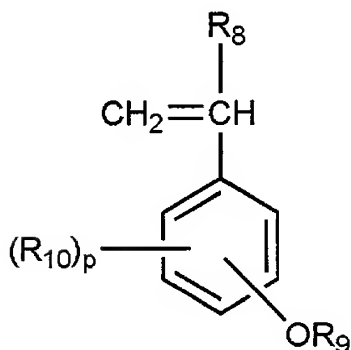


Formula (III)

(wherein, R₆ is hydrogen or methyl, and R₇ is a group having a t-butyl group and to be eliminated and/or decomposed with an acid), of which Components (A) and (B) are bound in block in the form of (A) - (B), has a ratio (M_w/M_n) of the weight-average molecular weight (M_w) to the number-average molecular weight (M_n) in a range of 1.00 and 1.50, and has no carboxylic acid residues.

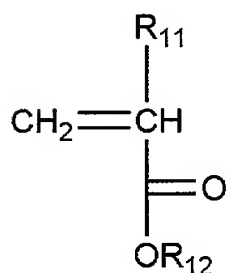
2. An alkenylphenol copolymer according to Claim 1 in which the weight-average molecular weight is 1,000 to 100,000.

3. A process for the preparation of the alkenylphenol copolymer according to Claim 1 or 2 in which a compound represented by Formula (IV) whose hydroxyl group of the phenol residue is protected



Formula (IV)

(wherein, R₈ is hydrogen or methyl, R₉ is a group to be eliminated and/or decomposed with an acid, R₁₀ is alkyl having 1 to 5 carbons, p is 0, 1 or 2 and R₁₀ is the same or different when p is 2) is polymerized, or a compound of Formula (IV) and a vinylaromatic compound are copolymerized, by anionic polymerization using an anionic polymerization initiator as a polymerization initiator, followed by copolymerization with a (meth)acrylic ester represented by Formula (V)



Formula (V)

(wherein, R₁₁ is hydrogen or methyl, and R₁₂ is a group having a t-butyl group and to be eliminated and/or decomposed with an acid); and the obtained block copolymer is treated with an acid reagent to eliminate and/or decompose only a specified amount of the group protecting the phenolic hydroxyl group.

4. A process for the preparation of the alkenylphenol copolymer according to Claim 3 in which the step of eliminating and/or decomposing only a specified amount of the group protecting the phenolic hydroxyl group with an acid reagent is carried out at below 60°C.

ABSTRACT

An ESCAP type polymer which has a controlled structure wherein the groups protecting phenolic hydroxyl groups have been selectively or partly eliminated or decomposed with an acid and no carboxylic acid residues are contained and which is a narrow-disperse polymer and is suitable for use as a material for a chemical amplification type resist for excimer lasers which has excellent resolution. The process is characterized by subjecting either an alkenylphenol in which the phenolic hydroxyl group has been protected or the alkenylphenol and a vinylaromatic compound to anionic polymerization together with a (meth)acrylic ester to give a block copolymer and eliminating only a given proportion of the groups protecting the phenolic hydroxyl groups from the block copolymer with an acid reagent. Thus, an alkenylphenol copolymer is synthesized which has a ratio of the weight-average molecular weight (M_w) to the number-average molecular weight (M_n), (M_w/M_n), of 1.00 to 1.50 and has no carboxylic acid residues.

Practitioner's Docket No. 1576.98**PATENT****COMBINED DECLARATION AND POWER OF ATTORNEY****(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL,
CONTINUATION, OR C-I-P)**

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type :

☐ original☒ national stage of PCT☐ divisional☐ design☐ continuation☐ supplemental☐ continuation in part**INVENTORSHIP IDENTIFICATION**

My RESIDENCE/POST OFFICE address and citizenship are as stated below, next to my name. I believe that I am the original, first and sole inventor of the subject matter that is claimed, and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

ALKENYLPHENOL COPOLYMER AND PROCESS FOR PRODUCING THE SAME

SPECIFICATION IDENTIFICATION

The specification is attached hereto.

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, Section 1.56, and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent.

PRIORITY CLAIM (35 U.S.C. Section 119(a)-(d))

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at

least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

Such applications have been filed as follows.

**PRIOR PCT APPLICATION(S) FILED WITHIN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION
AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. SECTION 119(a)-(d)**

COUNTRY (INDICATE IF PCT)	APPLICATION NUMBER	DATE OF FILING DAY, MONTH, YEAR	PRIORITY CLAIMED UNDER 35 USC 119
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

POWER OF ATTORNEY

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

APPOINTED PRACTITIONER(S)

REGISTRATION NUMBER(S)

Joseph C. Mason, Jr.

20,153

Dennis G. LaPointe

40,693

Louise A. Foutch

37,133

SEND CORRESPONDENCE TO

DIRECT TELEPHONE CALLS TO:

Mason & Associates, P.A.
17757 U.S. Hwy 19 North
Suite 500
Clearwater, FL 33764

727-538-3800

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

Full name of sole or first inventor

INVENTOR			Country of of Citizenship
Given Name	Middle Initial	Family (Last) Name	
Hitoshi		MATSUMOTO	Japan

RESIDENCE/Post Office Address	CITY	Country
Room No.907, 3-18-2, Oyumino, Midori-ku, Chiba-shi	Chiba	Japan JPX

Inventor's Signature: Hitoshi Matsumoto

Date: Feb-7th-2002

Full name of second joint inventor, if any

INVENTOR			Country of of Citizenship
Given Name	Middle Initial	Family (Last) Name	
Yukikazu		NOBUHARA	Japan

RESIDENCE/Post Office Address	CITY	Country
Room No.3-306, 2792-1, Goi, Ichihara-shi	Chiba	Japan

Inventor's Signature: Nobuhara Nobuhara

Date: Feb. 13. 2002

Full name of third joint inventor, if any

INVENTOR			Country of of Citizenship
Given Name	Middle Initial	Family (Last) Name	
Shinichi		KIMIZUKA	Japan

RESIDENCE/Post Office Address	CITY	Country
995-26, Shiizu, Ichihara-shi,	Chiba	Japan JPX

Inventor's Signature: Shinichi Kimizuka

Date: Feb. 13. 2002

(check proper box(es) for any of the following added page(s) that form a part of this declaration)

- ☐ Signature for fourth and subsequent joint inventors. Number of pages added: ____.
- ☐ Signature by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. Number of pages added: ____.
- ☐ Signature for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR 1.47. Number of pages added: ____.
- ☐ Added page for signature by one joint inventor on behalf of deceased inventor(s) where legal representative cannot be appointed in time. (37 CFR 1.47)
- ☐ Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (C-I-P) application. ☐ Number of pages added: ____.

**ADDED PAGE TO COMBINED DECLARATION
AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION
OR C-I-P APPLICATION**

**CLAIM FOR BENEFIT OF EARLIER U.S./PCT APPLICATION(S)
UNDER 35 U.S.C. SECTION 120**

I hereby claim the benefit, under Title 35, United States Code, Section 120, of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose information that occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application.

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. SECTION 120:				
U.S. APPLICATIONS		Status		
U.S. APPLICATIONS	U.S. FILING DATE	Patented	Pending	Abandoned
PCT APPLICATION DESIGNATING THE U.S.				
PCT APPLICATION NO.	PCT FILING DATE	U.S. APPLICATION NOS. ASSIGNED (IF ANY)		
PCT/JP00/05958	01 September 2000 (01.09.00)		X	

**ALL FOREIGN APPLICATION(S), IF ANY, FILED MORE THAN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION**

Country	Application No.	Filing Date
JAPAN	11/250861	03 September 1999 (03.09.99)

(Added Page to Combined Declaration and Power of Attorney
Page 4 of 4)

Express Mail: EV 032346025 US

Mailed: 01 March 2002